UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5

DATE: October 27, 2009

SUBJECT: PAH Benchmarks in Soil and Sediment, Former West Tar Products Site, Terre Haute, Indiana

FROM: James Chapman, Ph.D., Ecologist

TO: Verneta Simon, OSC

Summary

A range of screening values corresponding to no effect and low effect levels are provided for total PAHs in soil and sediment. The benchmarks are not enforceable clean up goals. Their primary purpose is to determine whether ecological risk can be ruled out, and, if not, to trigger further site-specific investigations. Benchmarks can be selected as clean up goals with the concurrence of all parties involved in decision-making at a site, for example, if the expense and effort of further investigations are considered unreasonable relative to the expected action. However, if challenged, use of benchmarks for clean up objective is not defensible.

Additional uncertainties are associated with comparisons of the benchmarks presented in this memo and site data because of the very limited sampling effort. PAHs were detected in one soil sample collected from underneath a tar flow, so there is no information on how the concentration or composition of PAHs may vary in contaminated soils. Out of necessity, the same sample is used as a surrogate for contaminated sediment with the assumption that the composition and concentrations of PAHs in sediment affected by tar flows would be similar to that in the one sample of contaminated soil. The U.S. EPA's preferred approach for calculating a sediment benchmark for PAHs requires site-specific data on the composition and concentrations of PAHs in sediment. Since only soil data are available, the sediment benchmark is referred to as an "example" benchmark. An additional complication is, in the absence of sediment data, an assumed value for sediment total organic carbon (OC) is used for 2 sets of sediment benchmarks. Site-specific sediment data are needed to calculate more valid site-specific sediment benchmarks.

The total PAH benchmarks for soil are 2.4 and 12 mg/kg dw, the no-effect soil benchmark is based on the U.S. EPA ecological soil screening level (Eco-SSL) for high molecular weight PAHs and mammalian wildlife (U.S. EPA 2007), adjusted for the PAH composition at the site, and the low-effect soil benchmark is derived from information presented in the same source.

The example calculation of a sediment total PAH benchmark is 6.8 mg/kg dw, based on an equilibrium partitioning approach for PAH mixtures and effects on benthic organisms (U.S. EPA 2003), site soil data, and an assumed 1 % sediment OC. This represents a no-effect sediment benchmark. A similar value, 7.3 mg/kg dw total PAHs, based on Canadian sediment quality guidelines (CCME 2002) and the PAH composition of the site soil sample (but not requiring sediment organic carbon data), represents a probable-effect benchmark (adverse effects

frequently expected). A third approach, not requiring data on PAH composition, but requiring the same assumption for sediment OC, results in 3 benchmarks for total PAHs: 2.9 mg/kg dw (no effect), 100 mg/kg dw (virtual certainty of adverse effects), and 18 mg/kg dw (middle likelihood of adverse effects).

Site Data

Ten polycyclic aromatic hydrocarbons (PAHs) were detected in a soil sample collected directly under a tar flow for a total PAH of 39.4 mg/kg dw, consisting of 17.9 mg/kg high molecular weight (HMW) PAHs (anthracene, benzo(a)anthracene, chrysene, indeno(1,2,3-cd)pyrene, and pyrene) and 21.4 mg/kg low molecular weight (LMW) PAHs (acenaphthylene, 2-chloronaphthalene, fluoranthene, flourene, and phenanthrene) (ENVision sample number 9-10005, Crum 2009).

Soils

Soil screening values for PAHs are listed in Table 1. There are separate U.S. EPA ecological soil screening levels (Eco-SSLs) for low molecular weight (LMW) PAHs, with less than 4 rings, and high molecular weight (HMW) PAHs, with 4 or more rings, to reflect broad differences in toxicity and exposure (U.S. EPA 2007). Since there are no Eco-SSLs for total PAHs, site-specific total PAH soil screening values are calculated based on the ratio of HMW PAHs and total PAH in site soil.

Table 1. Soil Screening Values for PAHs

Type	Receptor	PAH	Value	Reference
Eco-SSL	Soil Invertebrates	LMW	29 mg/kg dw	U.S. EPA 2007
	Mammalian Wildlife		100 mg/kg dw	
	Soil Invertebrates	HMW	18 mg/kg dw	
	Mammalian Wildlife		1.1 mg/kg dw	
Site-specific Eco-SSL		Total	2.4 mg/kg dw	Derived for site [a]
LOAEL-based Screening Level	Mammalian Wildlife	HMW	5.5 mg/kg dw	Derived from U.S. EPA 2007
Site-specific LOAEL-bassed Screening Level		Total	12 mg/kg dw	Derived for site [b]

Table 1 Notes:
Type: Eco-SSL – ecological soil screening level, LOAEL – lowest observed adverse effect level
PAH: polycyclic aromatic hydrocarbon, LMW – low molecular weight, HMW – high molecular weight
Value: dw – dry weight
a) Site-specifc Eco-SSL = 1.1 mg HMW/kg dw * (Total PAH conc. / HMW conc.)
Total PAH conc. / HMW conc. = 39.4 / 17.9 (ENVision sample number 9-10005, Crum 2009)
b) Site-specifc LOAEL-based Screening Level = 5.5 mg HMW/kg dw * (Total PAH conc. / HMW conc.)

The sample concentration of LMW PAHs is less than the ecological soil screening levels (Eco-SSLs) for soil invertebrates (29 mg/kg dw) and mammalian wildlife (100 mg/kg dw) (U.S. EPA 2007). The sample concentration of HMW PAHs is equal to the Eco-SSL for soil invertebrates (18 mg/kg dw), but is an order-of-magnitude greater than the Eco-SSL for mammalian wildlife (1.1 mg/kg dw) (U.S. EPA 2007). This indicates that the LMW PAHs of the sample are unlikely to present risks to soil invertebrates or mammals, or the HMW PAHs to soil invertebrates. In contrast, mammals may be potentially at risk from exposure to HMW PAHs.

The Eco-SSLs are based on no observed adverse effect levels (NOAEL), however, lowest observed adverse effect level (LOAEL) data are also compiled. The HMW PAH Eco-SSL for mammalian wildlife is based on a NOAEL for survival of 0.615 mg PAHs/kg_{BW}-d (milligrams per kilogram bodyweight per day) selected as the highest bounded NOAEL that is lower than the lowest bounded LOAEL in the PAH Eco-SSL database of mammalian studies. A "bounded" value is when both a NOAEL and LOAEL are reported in a single study. The lowest bounded LOAEL (that delineated the Eco-SSL mammalian NOAEL) was 3.07 mg PAHs/kg_{BW}-d (U.S. EPA 2007), which, assuming linearity, corresponds to a LOAEL-based soil benchmark of 5.5 mg/kg dw HMW PAHs. The sample HMW PAH concentration exceeds the LOAEL-based soil benchmark by more than 3-fold, a further indication that the HMW PAHs might present unacceptable risk to mammals.

Site-specific total PAH soil screening levels of 2.4 and 12 mg/kg dw correspond to the Eco-SSL of 1.1 mg/kg dw HMW PAHs and the LOAEL-based soil screening level of 5.5 mg/kg dw HMW PAHs, respectively, based on the composition of PAHs in the soil sample collected directly under the tar flow (ENVision sample 9-10005, Crum 2009).

Sediment

Sediment screening values for PAHs for protection of benthic organisms are listed in Table 2. The recommended U.S. EPA procedure for deriving an equilibrium partitioning sediment benchmark (ESB) for total PAHs is dependent on the site-specific composition of PAHs in sediments and the sediment total organic carbon (OC) content (U.S. EPA 2003). Data on the composition of PAHs are required because the benchmark is based on narcosis toxicity due to the combined effect of each PAH individually evaluated. Narcosis is "a generalized depression in biological activity" associated with disruption of cellular membrane functions (Rand, et al. 1995). The toxicity of a chemical causing Type I (nonpolar) narcosis is proportional to its octanol:water partition coefficient (K_{ow}), and the effect of multiple chemical exposures are additive (Veith and Broderius 1990).

Site-specific sediment data are not available to perform the ESB calculation, so, instead, an example calculation is shown using the PAH composition of the soil sample collected directly under the tar flow and assuming a sediment OC content of 1 %. A second set of sediment PAH benchmarks is included that does not depend on the site-specific PAH composition (Swartz 1999), however, a 1 % sediment OC content is assumed to convert the organic carbon-normalized benchmarks to whole sediment PAH concentrations. Both the U.S. EPA (2003) and Swartz (1999) whole-sediment benchmarks will need to be recalculated for the actual sediment OC content at the site when available. For comparison, Canadian freshwater sediment benchmarks for individual PAH compounds are also included in Table 2 because the values are given on a whole-sediment basis (Canada has not developed total PAH sediment screening values) (CCME 2002).

Table 2. Sediment Screening Values for PAHs Based on Effects on Benthic Invertebrates					
Country	**Type**	**PAH**	**Normalized Value** (mg/kg OC)	**Whole-sed Value** (mg/kg dw)	**Reference**
U.S.	Example Site-specific ESB	Total	680 [a]	6.8 [a]	U.S. EPA 2003
U.S.	Consensus TEC	Total	290	2.9 [b]	Swartz 1999
	Consensus MEC		1800	18 [b]	
	Consensus EEC		10000	100 [b]	
Canada	ISQC	Benzo(a)anthracene		0.0317	CCME 2002
	PEL			0.385	
	ISQC	Chrysene		0.0571	
	PEL			0.862	
	ISQC	Fluoranthene		0.111	
	PEL			2.355	
	ISQC	Phenanthrene		0.0419	
	PEL			0.515	
	ISQC	Pyrene		0.053	
	PEL			0.875	

Table 2 Notes:
Type: ESB – equilibrium partitioning sediment benchmark (no observed adverse effect level), TEC – threshold effects concentration (effect unlikely), MEC – median effects concentration (middle of gradient from no to extreme effects), EEC – extreme effects concentration (virtual certainty of adverse effects). ISQC – interim freshwater sediment quality guideline (adverse effects expected rarely, <25 % incidence), PEL – probable effect level (adverse effects expected frequently, >50 % incidence)
PAH – polycyclic aromatic hydrocarbon
Normalized Value: OC – organic carbon
Whole-sed Value: sed – sediment, dw – dry weight
a) Calculated using soil PAH data and assuming 1 % OC in sediment (Appendix 1)
b) Calculated from Normalized Value assuming 1 % OC.

The following comparisons are based on 2 key assumptions: 1) the composition and concentration of PAHs in sediment affected by tar flows are similar to those reported in soil directly below a tar flow, and 2) the sediment total organic carbon is approximately 1 % dw.

With the aforementioned assumptions, the example site-specific ESB for total PAHs is 680 mg/kg OC, and, on a whole-sediment basis, 6.8 mg/kg dw, which is much lower than the site soil sample 39.4 mg/kg dw total PAH concentration. The U.S. EPA (2003) ESB is based on an equilibrium partitioning (EqP) approach using aquatic no observed adverse effect level (NOAEL) data.

The consensus sediment quality guidelines (SQG) by Swartz (1999) are calculated as the arithmetic mean of existing PAH sediment screening values by 3 levels of effect: threshold effects concentration (TEC) (adverse effects are unlikely), median effects concentration (MEC) (middle of gradient between no and extreme adverse effects), and extreme effects concentration (EEC) (virtual certainty of adverse effects). Assuming 1 % TOC in sediment, the TEC (2.9 mg/kg dw total PAHs) in which adverse effects are not expected is within about a factor of 2 of the example site-specific ESB. The total PAH concentration of the site soil sample is greater than the MEC (18 mg/kg dw) that indicates the mid-range likelihood of adverse effects, but is less than the EEC for virtual certainty of adverse effects.

Canadian sediment quality guidelines for individual PAHs in freshwater sediment are included because they are given for whole-sediment (CCME 2002), and therefore do not depend on the 2nd assumption (sediment OC). The guidelines are based on an empirical database of field measurements of matched sediment contaminant and biological data. Since individual PAHs are not present in isolation in the environment, but occur with other PAHs that act jointly to cause toxicity, the Canadian guideline for any one PAH represents the sediment concentration of that PAH necessary so that the combined toxic effect of all the likely co-occurring PAHs is unlikely to cause unacceptable risk. This means that the individual PAH guidelines are not added together, and, likewise, individual hazard quotients should not be summed. The concentrations of the site soil sample PAHs corresponding to the available Canadian freshwater sediment guidelines are (mg/kg dw): benzo(a)anthracene (4.16), chrysene (2.85), fluoranthene (12.7), phenanthrene (5.41), and pyrene (8.17) (Crum 2009). All of these exceed both the interim sediment quality guidelines (ISQG) for which adverse effects are rarely expected, and the probable effect levels (PEL) for which adverse effects are frequently expected. The site soil PAH concentrations exceed the respective PELs by 3- to 11-fold. Since fluoranthene has the highest concentration of the PAHs considered here, it may provide the most reliable estimate. The site soil fluoranthene concentration exceed the PEL by 5-fold, and, based on the site soil sample PAH composition, a total PAH PEL for the site would be 7.3 mg/kg dw, similar to the example site-specific ESB. The total PAH PEL indicates adverse effects may be likely but the example site-specific ESB is calculated for no observed adverse effects. Both benchmarks are intermediate between the consensus TEC (adverse effects unlikely) and MEC (mid-range likelihood of adverse effects).

Literature Cited

CCME. 2002. Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. Updated. Canadian Council of Ministers of the Environment, Winnipeg. http://ceqg-rcqe.ccme.ca/

Crum, C. 2009. ENVision Project Number: 2009-1424, Client Project Name: 3268B / Cavu-Ops Wabash. July 27, 2009 memo from Cheryl Crum, ENVision Laboratories, Inc. to Scott Randall, Keramide Environmental, Inc.

Rand, G., P. Wells, and L. McCarty. 1995. Introduction to aquatic toxicology. *In:* Fundamentals of Aquatic Toxicology: Effects, Environmental Fate, and Risk Assessment, 2nd ed. (Ed.: G. Rand). Taylor & Francis, Washingon, D.C. pp. 3-67.

Swartz, R. 1999. Consensus sediment quality quidelines for polycyclic aromatic hydrocarbon mixtures. Environ Toxicol Chem 18: 780-787.

U.S. EPA. 2003. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures. Office of Research and Development. EPA-600-R-02-013. www.epa.gov/nheerl/publications/

U.S. EPA. 2007. Ecological Soil Screening Levels for Polycyclic Aromatic Hydrocarbons

(PAHs), Interim Final. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. OSWER Directive 9285.7-78. www.epa.gov/ecotox/ecossl/

Veith, G. and S. Broderius. 1990. Rules for Distinguishing Toxicants That Cause Type I and Type II Narcosis Syndromes. Environ Health Perspect 87: 207-211.

Appendix 1. Example Calculation of a Site-specific Equilibrium Partitioning Sediment Benchmark Using PAH Data from Soil Directly Under a Tar Flow at the Former West Tars Site, Terre Haute, Indiana, and Assuming 1 % Organic Carbon in Sediment.

PAH	C_{PAH} mg/kg dw	OC % dw	$C_{OC,PAH}$ mg/kg OC	$C_{OC,PAH,FCV}$ mg/kg OC	$ESTBTU_{FCV}$ ratio
Acenaphthylene	1.39	1.0	139	452	0.308
Anthracene	1.48	1.0	148	594	0.249
Benzo(a)anthracene	4.16	1.0	416	841	0.495
2-Chloronaphthalene	1.20	1.0	120	444	0.270
Chrysene	2.85	1.0	285	826	0.345
Fluoranthene	12.70	1.0	1270	707	1.796
Fluorene	0.72	1.0	72	538	0.134
Indeno(1,2,3-cd)pyrene	1.27	1.0	127	1115	0.114
Phenanthrene	5.41	1.0	541	596	0.908
Pyrene	8.17	1.0	817	697	1.172
Total PAHs	39.35	1.0	3935	**$\sum ESTBTU_{FCV}$**	**5.79**

Example site-specific normalized sediment benchmark	680	mg/kg OC
Example site-specific whole-sediment benchmark	6.8	mg/kg dw

Appendix 1 Notes:

PAH – polycyclic aromatic hydrocarbon

C_{PAH} – whole-sediment PAH concentration (soil surrogate: ENVision Sample 9-10005, collected 7/13/09, Crum 2009)

OC – sediment total organic carbon (assumed value), dw – dry weight

$C_{OC,PAH}$ – organic carbon-normalized PAH concentration = C_{PAH} / (OC / 100)

$C_{OC,PAH,FCV}$ – critical PAH organic carbon-normalized concentration in sediment corresponding to the Final Chronic Value (Table 3-4 in U.S. EPA. 2003)

FCV – final chronic value

$ESTBTU_{FCV}$ – equilibrium partitioning sediment benchmark toxic unit = $C_{OC,PAH}$ / $C_{OC,PAH,FCV}$

$\sum ESTBTU_{FCV}$ – total equilibrium partitioning sediment benchmark toxic units

Example site-specific normalized sediment benchmark = total $C_{OC,\ PAH}$ / $\sum ESTBTU_{FCV}$

Example site-specific whole-sediment benchmark = total C_{PAH} / $\sum ESTBTU_{FCV}$